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Description

The present invention relates to polymer blends and articles prepared therefrom.

Liquid storage containers blow-moulded from polyesters, particularly poly(ethylene terephthalate) are easily fabricated at reasonable cost and have received wide acceptance in the market place as containers suitable for storing many liquids. The use of such polyester containers to package liquids having a sensitivity to oxygen or liquids requiring internal pressurization by the addition of carbon dioxide has been somewhat restricted, however, by reason of the fact that most polyesters, and particularly poly(ethylene terephthalate), allow significant ingress of environmental oxygen and significant egress of carbon dioxide to and from the package contents. In many circumstances like soft drink packaging, beer packaging and wine packaging, the barrier characteristics have significantly reduced the utility of polyester based containers.

In the past, a number of approaches have been used to attempt to solve the poor barrier properties of polyester resins. Various barrier polymers have been admixed with polyesters in an attempt to improve container performance. Unfortunately, resin expense or only marginally superior results in respect of physical properties and barrier characteristics compared to native polyesters have been experienced. Notably, such admixtures show significant moisture sensitivity and are not optically clear when blow moulded.

Similarly, many chemically modified polyesters have been developed in an attempt to overcome the relatively poor barrier properties of the polyesters by adding various functional groups to the polymer chain. Unfortunately, costs, or processing characteristics, poor barrier properties or poor mechanical strength have significantly reduced the acceptance of these materials in the market place.

Accordingly, there is a need in the art for an improved polyester-based resin blend which is capable of being injection-moulded, providing a high gas and water vapour transmission barrier, excellent mechanical properties, low sensitivity to barrier performance loss when exposed to moisture, low acetaldehyde levels upon processing for use of foodstuffs as well as being optically clear when blow-moulded and capable of being strain-hardened upon molecular orientation by blow-moulding.

According to the present invention there is provided a composition characterised by:

an intimate fusion blend of:

- (1) 80 to 90 weight percent of a poly(ethylene terephthalate); and
- (2) 10 to 20 weight percent of a copolyester formed of the polymeric reaction product of,
 - (A) reactant(s) selected from isophthalic acid, terephthalic acid, and their C₁ to C₄ alkyl esters, and any mixture thereof in any proportion,
 - (B) reactants, 1,2 bis(2 - hydroxyethoxy) benzene plus ethylene glycol, wherein the amount of the 1,3 bis(2 - hydroxyethoxy)benzene is 5 to 90 mol percent of the amount of (A) reactants.

The present invention also provides a sheet or film and also a deep drawn tray having the composition of the fusion blend of the present invention.

In accordance with one embodiment of the present invention there is provided a container comprising (a) an open top portion, (b) an enclosed main body portion integral with and downwardly depending from the open top portion, and (c) an enclosed bottom portion integral with and downwardly depending from the enclosed main body portion, the container being fabricated from the fusion blend of the present invention.

In accordance with another embodiment of the present invention there is provided a container preform comprising (a) a threaded finish portion, (b) a main body portion integral with and downwardly depending from the threaded finish portion, and (c) a closed bottom portion integral with and downwardly depending from the main body portion, the preform being fabricated from the fusion blend of the present invention.

The present invention provides an intimate fusion blend of two different polyester materials in the indicated ranges of proportions having an advantageous balance of mechanical properties and gas and water barrier making the new intimate fusion blend well-suited for conversion into container parisons and a variety of container shapes by blow-moulding as well as thermoforming of films into packaging. The polyester-based intimate fusion blend materials according to the present invention are injection-mouldable, provide excellent gas and moisture barrier, maintain mechanical properties and are optically clear upon blow-moulding in addition to producing very low levels of acetaldehyde during blow-moulding at conventional processing temperatures. Also, the new material can be oriented and is strain-hardenable during orientation blow-moulding conditions to produce excellent rigid containers. Further, upon exposure to moisture, the material does not exhibit a significant decline in gas barrier properties.

The polyester-based intimate fusion blended composition according to the present invention comprise an admixture of a poly(ethylene terephthalate) and a copolyester in specific ranges of proportions. The preferred copolyester material is a copolyester of isophthalic or terephthalic acid, ethylene glycol and 1,3 bis(2 - hydroxyethoxy)benzene. The composition may also include small amounts of bis (4 - beta - hydroxyethoxyphenyl) sulfone when it is desired to elevate the glass transition temperature of the copolyester component of the blend.

The intimate fusion blends according to the present invention are suitable for forming injection moulded container parisons and the hollow containers therefrom, particularly by blow-moulding of bottles or thermoforming for deep drawn food trays or for producing sheetstock or film, all having excellent barrier

properties, mechanical strength and processability with low acetaldehyde levels. The new composition can be conveniently used to make small containers by injection blow moulding or larger containers by injection, cool, reheat and blow techniques. The material when used to injection-blow mould small containers without the induction of significant amounts of molecular orientation shows barrier properties with respect to CO₂ and O₂ transmission, as well as water vapour transmission, comparable to biaxially oriented poly(ethylene terephthalate). In the use where parisons are injection moulded, cooled for storage and subsequently reheated to orientation temperature and blow moulded to induce molecular orientation the resultant containers show significantly improved CO₂ and O₂ barrier as compared to conventional biaxially oriented poly(ethylene terephthalate) containers of equivalent size, shape and thickness characteristics.

The present invention will be more particularly described hereinafter with reference to and as illustrated in, but in no manner limited to the accompanying drawings, in which:

Figure 1 is a graphical representation of the CO₂ gas transmission characteristics of poly(ethylene terephthalate) and copolyester compared to the compositions according to the invention;

Figure 2 is a graphical representation of the O₂ gas transmission characteristics of poly(ethylene terephthalate) and copolyester compared to the compositions according to the invention;

Figure 3 is a perspective view of a parison according to the present invention;

Figure 4 is a perspective view of one embodiment of a container according to the present invention, namely a bottle; and

Figure 5 is a perspective view of another embodiment of a container according to the present invention, namely a deep drawn food tray.

The polyester-based intimate fusion blend compositions according to the present invention comprise an admixture of 80 to 90 weight percent of a poly(ethylene terephthalate), hereinafter referred to as PET, and 10 to 20 weight percent of copolyester.

The preferred PET material, according to the present invention is formed from the reaction between ethylene glycol and terephthalic acid or an ester thereof, particularly dimethyl terephthalate, and has an inherent viscosity of at least 0.6. Other PET materials useful herein are poly(ethylene terephthalate) polymers including polymers where at least 97% of the polymer contains the repeating ethylene terephthalate units with the remainder being minor amounts of ester-forming components, and copolymers of ethylene terephthalate wherein up to about 10 mole percent of the polymer is prepared from the monomer units are selected from butane - 1,4 - diol; diethylene glycol; propane - 1,3 - diol; poly(tetramethylene glycol); poly(propylene glycol); 1,4 - hydroxymethylcyclohexane and the like, substituted for the glycol moiety in the preparation of the polymer, or isophthalic; naphthalene, 1,4- or 2,6 - dicarboxylic; adipic; sebacic; decane - 1,10 - dicarboxylic acids, and the like, substituted for up to 10 mole percent of the acid moiety (terephthalic acid) in preparation of the polymer.

Of course, the poly(ethylene terephthalate) polymer can include various additives that do not adversely affect the polymer. For instance, some such additives are stabilizers, e.g., antioxidants or ultraviolet light screening agents, extrusion aids, additives designed to make the polymer more degradable or combustible, and dyes or pigments. Moreover, cross-linking or branching agents such as are disclosed in U.S. Patent No. 4,188,357 can be included in small amounts in order to increase the melt strength of the poly(ethylene terephthalate).

The copolyesters, which form the polyester-based intimate fusion blend composition when admixed with PET according to the present invention, are copolyesters based on terephthalic or isophthalic acid or both, ethylene glycol and which contain 1,3 bis(2 - hydroxyethoxy)benzene as one of the diol reactants in order to prepare the solid copolyesters for admixture with PET.

The solid thermoplastic copolyesters are formed of the polymeric reaction product of:

(A) reactant(s) selected from isophthalic acid, terephthalic acid, and their C₁ to C₄ alkyl esters, and any mixture thereof in any proportion,

(B) reactants, 1,3 bis(2 - hydroxyethoxy)benzene plus ethylene glycol, and optionally one or more other ester forming dihydroxy organic hydrocarbon reactant(s), and, optionally,

(C) reactant, bis(4 - beta - hydroxyethoxyphenyl) sulfone, wherein:

(1) the amount of said 1,3 bis(2 - hydroxyethoxy)benzene is 5—90 mole percent of the amount of (A) reactants, usually not less than 10 or more than 80, mole percent of the amount of (A) reactants,

(2) the combined amount of (B) and (C) reactant is about 110 to 300 mole percent of the amount of (A) reactants,

(3) the amount of said other ester forming dihydroxy organic hydrocarbon reactant(s) is zero to 20, usually zero to 15, mole percent of the amount of said (A) reactants, and

(4) the combined amount of said (C) reactant plus said 1,3 bis(2 - hydroxyethoxy)benzene and said other ester forming dihydroxy organic hydrocarbon reactant(s) is not over 90 mole percent of said (A) reactants.

In the foregoing copolyesters the optional (C) reactant, bis(4 - beta - hydroxyethoxyphenyl) sulfone, is used when it is necessary to raise the glass transition temperature of the copolyester composition portion of the PET-copolyester blend composition for a particular application.

When less than 5 mol percent of 1,3 bis(2 - hydroxyethoxy) benzene is used, the effect on

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permeabilities is not as significant as desired. When over 90 mol percent is used, the reaction or polycondensation rate is lower than desired.

The copolyesters so produced are solid copolyesters having an inherent viscosity of at least about 0.4 dl/g., usually at least 0.5 and for most commercial applications, at least 0.7 dl/g. The inherent viscosities referred to herein are those measured at 25°C., using a solution of 0.25 gms. of polymer dissolved in 100 millilitres of a mixture of 3 weight parts phenol with 2 weight parts 1,1,2,2 tetrachloroethane.

The glass transition temperature, T_g , was determined using a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-2, in a manner similar to that described in U.S. Patent No. 3,822,322, issued July 2, 1974, using a heating rate of 10°C/minute.

The following Examples are illustrative of the formation of the polyesters according to the present invention.

Example 1

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

233 g	dimethyl terephthalate
167.6 g	ethylene glycol
59.4 g	1,3 bis(2-hydroxyethoxy)benzene
0.0660 g	titanyl acetylacetonate
0.0874 g	Sb_2O_3
0.0303 g	manganese hypophosphite monohydrate
0.0114 g	tetrasodium ethylenediaminetetraacetate
0.4325 g	1,1,1 tris hydroxymethyl ethane.

The reaction mixture was heated at 200°C for 1 hour and 20 minutes under nitrogen atmosphere. Methanol was continuously distilled out during this period. Then 0.4128 g of tris(nonylphenyl)phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C and maintained for 1 hour under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.4 mm Hg was applied. The reaction was continued at 275°C under less than 0.053 kPa (0.4 mm Hg) for 2 hours 50 minutes. The copolyester had an inherent viscosity of 0.86 dl/g. The glass transition temperature was 72°C. The O_2 and CO_2 gas permeabilities were 26.55×10^{-12} and 161.1×10^{-12} cc-mm/cm²-sec-kPa (5.9 and 35.8 cc./mil per 100 in.²/day/atm.), respectively.

Example 2

Poly(ethylene terephthalate) was prepared as follows:

Into a 500 ml 3-necked round bottom flask, equipped with a nitrogen gas inlet tube, stirrer and a condenser, the following compounds were added:

46.5 g	dimethyl terephthalate
35.4 g	ethylene glycol
0.0263 g	zinc acetate dihydrate
0.01398 g	antimony trioxide.

The contents of the flask were heated at 220°C under nitrogen atmosphere for 3 hours. During this time, methanol was distilled off. Then the reaction temperature was raised to 280°C., nitrogen flow was stopped and vacuum was gradually applied until less than 0.067 kPa (0.5 mm Hg). Excess ethylene glycol was continuously distilled off. The reaction was stopped after 4 hours. The inherent viscosity was 0.83, the glass transition temperature was 72°C., the oxygen permeability was 38.25 cc-mm/cm²-sec-kPa (8.5 cc./mil per 100 in.²/day/atm.) and the carbon dioxide permeability was 248.85 cc-mm/cm²-sec-kPa (55.3 cc./mil per 100 in.²/day/atm.).

Example 3

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

233.0 g	dimethyl terephthalate
134.1 g	ethylene glycol
166.3 g	1,3 bis(2-hydroxyethoxy)benzene
0.4325 g	1,1,1 tris(hydroxymethyl)ethane
0.0114 g	titanyl acetylacetonate
0.0874 g	Sb_2O_3
0.0114 g	tetrasodium ethylenediaminetetraacetate
0.0303 g	manganese hypophosphite monohydrate

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The reaction mixture was heated at 200°C for 1 hour under nitrogen atmosphere. Methanol was continuously distilled out during this period. Then 0.4128 g of tris (nonylphenyl)phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C and maintained for 55 minutes under nitrogen atmosphere. Then the nitrogen gas flow was applied. The reaction was continued at 270°C under less than 0.053 kPa (0.4 mm Hg) for 5.5 hours. The copolyester had an inherent viscosity of 0.65. The glass transition temperature was 64°C. The O₂ and CO₂ gas permeabilities were 17.1×10^{-12} and 100.8×10^{-12} cc-mm/cm²-sec-kPa (3.8 and 22.4 cc/mil per 100 in.²/day/atm.), respectively.

Example 4

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

	332.3 g	isophthalic acid
	192.2 g	ethylene glycol
15	19.8 g	1,3 bis(2-hydroxyethoxy)benzene
	0.1100 g	titanyl acetylacetonate
	0.1458 g	Sb ₂ O ₃
	0.0190 g	tetrasodium ethylenediaminetetraacetate
	0.7209 g	1,1,1 tris(hydroxymethyl)ethane

The reaction mixture was heated at 220°C for 1 hour, and then at 240°C for 40 minutes under nitrogen atmosphere. Water was continuously distilled out during this period. Then 0.688 g of tris (nonylphenyl) phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C and maintained for 50 minutes under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.053 kPa (0.4 mm Hg) was applied. The reaction was continued at 270°C under less than 0.053 kPa (0.4 mm Hg) for 3 hours 55 minutes. The copolyester had an inherent viscosity of 0.83. The glass transition temperature was 61°C. The O₂ and CO₂ gas permeabilities were 7.2×10^{-12} and 31.95×10^{-12} cc-mm/cm²-sec-kPa (1.6 and 7.1 cc/mil per 100 in.²/day/atm.), respectively.

Example 5

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

	332.3 g	isophthalic acid
35	180 g	ethylene glycol
	59.4 g	1,3 bis(2-hydroxyethoxy)benzene
	0.7209 g	1,1,1 tris(hydroxymethyl)ethane
	0.1100 g	titanyl acetylacetonate
	0.1458 g	Sb ₂ O ₃
40	0.019 g	tetrasodium ethylenediaminetetraacetate

The reaction mixture was heated at 220°C for 1 hour, and then at 240°C for 30 minutes under nitrogen atmosphere. Water was continuously distilled out during this period. Then 0.688 g of tris(nonylphenyl)-phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C and maintained for 40 minutes under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.053 kPa (0.4 mm Hg) was applied. The reaction was continued at 270°C under less than 0.053 kPa (0.4 mm Hg) for 4.5 hours. The copolyester had an inherent viscosity of 0.82. The glass transition temperature was 60°C. The O₂ and CO₂ gas permeabilities were 7.2×10^{-12} and 29.7×10^{-12} cc-mm/cm²-sec-kPa (1.6 and 6.6 cc/mil per 100 in.²/day/atm.), respectively.

Example 6

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

55	139.5 g	isophthalic acid
	59.8 g	terephthalic acid
	107.9 g	ethylene glycol
	35.6 g	1,3 bis(2-hydroxyethoxy)benzene
	0.4325 g	1,1,1 tris(hydroxymethyl)ethane
60	0.066 g	titanylacetonate
	0.0874 g	Sb ₂ O ₃
	0.0114 g	tetrasodium ethylenediaminetetraacetate
	0.0303 g	manganese hypophosphite monohydrate

The reaction mixture was heated at 220°C for 1 hour, and then at 240°C for 25 minutes under nitrogen

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atmosphere. Water was continuously distilled out during this period. The 0.1862 g of tris(nonylphenyl)-phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C and maintained for 35 minutes under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.053 kPa (0.4 mm Hg) was applied. The reaction was continued at 275°C under less than 0.053 kPa (0.4 mm Hg) for 4 hours 5 minutes. The copolyester has an inherent viscosity of 0.89. The glass transition temperature was 63°C. The O₂ and CO₂ gas permeabilities were 9.0×10^{-12} and 43.65×10^{-12} cc-mm/cm²-sec-kPa, respectively, (2.0 and 9.7 cc./mil per 100 in.²/day/atm., respectively).

Example 7

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

	139.5 g	isophthalic acid
	59.8 g	terephthalic acid
15	100.4 g	ethylene glycol
	35.6 g	1,3 bis(2-hydroxyethoxy)benzene
	40.6 g	bis(4-beta-hydroxyethoxyphenyl)sulfone
	0.4325 g	1,1,1 tris(hydroxymethyl)ethane
	0.0660 g	titanylacetylacetonate
20	0.0874 g	Sb ₂ O ₃
	0.0114 g	tetrasodium ethylenediaminetetraacetate
	0.0303 g	manganese hypophosphite monohydrate

The reaction mixture was heated at 200°C for 20 minutes, and then at 240°C for 50 minutes under nitrogen atmosphere. Water was continuously distilled out during this period. Then 0.4128 g of tris(nonylphenyl)phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C and maintained for 25 minutes under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.053 kPa (0.4 mm Hg) was applied. The reaction was continued at 270°C under less than 0.053 kPa (0.4 mm Hg) for 4 hours. The copolyester had an inherent viscosity of 0.77. The glass transition temperature was 72°C. The O₂ and CO₂ gas permeabilities were 11.25×10^{-12} and 58.05×10^{-12} cc-mm/cm²-sec-kPa (2.5 and 12.9 cc./mil per 100 in.²/day/atm.), respectively.

Example 8

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

	139.5 g	isophthalic acid
	59.8 g	terephthalic acid
40	100.4 g	ethylene glycol
	35.6 g	1,3 bis(2-hydroxyethoxy)benzene
	17.3 g	1,4 trans cyclohexanedimethanol
	0.0660 g	titanylacetylacetonate
	0.0874 g	Sb ₂ O ₃
	0.0114 g	tetrasodium ethylenediaminetetraacetate
45	0.0303 g	manganese hypophosphite monohydrate
	0.4325 g	1,1,1 tris(hydroxymethyl)ethane

The reaction mixture was heated at 200°C for 1 hour, and then at 240°C for 1 hour under nitrogen atmosphere. Water was continuously distilled out during this period. Then 0.4128 g of tris(nonylphenyl)-phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C and maintained for 30 minutes under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.053 kPa (0.4 mm Hg) was applied. The reaction was continued at 270°C under less than 0.053 kPa (0.4 mm Hg) for 4 hours. The copolyester had an inherent viscosity of 0.81. The glass transition temperature was 63°C. The O₂ and CO₂ gas permeabilities were 14.85×10^{-12} and 248.85×10^{-12} cc-mm/cm²-sec-kPa (3.3 and 15.3 cc./mil per 100 in.²/day/atm.), respectively.

Example 9

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

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	139.5 g	isophthalic acid
	59.8 g	terephthalic acid
	78.2 g	ethylene glycol
	35.6 g	1,3 bis(2-hydroxyethoxy)benzene
5	12.5 g	neopentyl glycol
	0.4325 g	1,1,1 tris(hydroxymethyl)ethane
	0.0660 g	titanylacetylacetonate
	0.0874 g	Sb ₂ O ₃
	0.0114 g	tetrasodium ethylenediaminetetraacetate
10	0.0303 g	manganese hypophosphite monohydrate

The reaction mixture was heated at 240°C for 1 hour under 241.33 kPa (35 psi) nitrogen atmosphere, and then the pressure was lowered to atmospheric. Water was continuously distilled out during this period. Then 0.4128 g of tris(nonylphenyl)phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C and maintained for 20 minutes under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.053 kPa (0.4 mm Hg) was applied. The reaction was continued at 270°C. under less than 0.053 kPa (0.4 mm Hg) for 4 hours. The copolyester had an inherent viscosity of 0.90. The glass transition temperature was 65°C. The O₂ and CO₂ gas permeabilities were 13.5×10⁻¹² and 45.9×10⁻¹² cc-mm/cm²-sec-kPa (3.0 and 10.2 cc./mil per 100 in.²/day/atm.), respectively.

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Example 10

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

25	179.4 g	isophthalic acid
	19.9 g	terephthalic acid
	78.2 g	ethylene glycol
	35.6 g	1,3 bis(2-hydroxyethoxy)benzene
	17.8 g	diethylene glycol
30	0.0660 g	titanylacetylacetonate
	0.0874 g	Sb ₂ O ₃
	0.4325 g	1,1,1 tris(hydroxymethyl)ethane
	0.0114 g	tetrasodium ethylenediaminetetraacetate
	0.0303 g	manganese hypophosphite monohydrate

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The reaction mixture was heated at 240°C for 1 hour under 241.33 kPa (35 psi) nitrogen atmosphere, and then the pressure was lowered to atmospheric. Water was continuously distilled out during this period. Then 0.4128 g of tris(nonylphenyl)phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C. and maintained for 20 minutes under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.053 kPa (0.4 mm Hg) was applied. The reaction was continued at 270°C under less than 0.053 kPa (0.4 mm Hg) for 5 hours. The copolyester had an inherent viscosity of 0.84. The glass transition temperature was 59°C. The O₂ and CO₂ gas permeabilities were 10.35×10⁻¹² and 50.85×10⁻¹² cc-mm/cm²-sec-kPa (2.3 and 11.3 cc./mil per 100 in.²/day/atm.), respectively.

45 Example 11

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

50	199.3 g	isophthalic acid
	89.4 g	ethylene glycol
	213.8 g	1,3 bis(2-hydroxyethoxy)benzene
	0.4325 g	1,1,1 tris(hydroxymethyl)ethane
	0.0660 g	titanylacetylacetonate
	0.0874 g	Sb ₂ O ₃
65	0.0114 g	tetrasodium ethylenediaminetetraacetate
	0.0303 g	manganese hypophosphite monohydrate

The reaction mixture was heated at 200°C for 1/2 hour, and then at 240°C for 1 hour under nitrogen atmosphere. Water was continuously distilled out during this period. Then 0.4128 g of tris(nonylphenyl)phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C. and maintained for 40 minutes under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.053 kPa (0.4 mm Hg) was applied. The reaction was continued at 275°C under less than 0.053 kPa (0.4 mm Hg) for 5.5 hours. The copolyester had an inherent viscosity of 0.45.

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Example 12

Into a 1-litre stainless steel reactor equipped with a stirrer, nitrogen gas inlet port and a condenser, the following were added:

5	224.3 g	isophthalic acid
	24.9 g	terephthalic acid
	148.9 g	ethylene glycol
	44.55 g	1,3 bis(2-hydroxyethoxy)benzene
	0.08253 g	titanyl acetylacetonate
10	0.10928 g	Sb ₂ O ₃
	0.5407 g	1,1,1 tris(hydroxymethyl)ethane
	0.01425 g	tetrasodium ethylenediaminetetraacetate
	0.03776 g	Mm (H ₂ PO ₂) ₂ ·2H ₂ O

15 The reaction mixture was heated at 240°C for 1 hour under 241.33 kPa (35 psi) nitrogen atmosphere, and then the pressure was lowered to atmospheric. Water was continuously distilled out during this period. Then 0.516 g of tris(nonylphenyl)phosphite was added to the mixture in the reactor. The reaction temperature was increased to 250°C and maintained for 20 minutes under nitrogen atmosphere. Then the nitrogen gas flow was stopped and a vacuum of less than 0.053 kPa (0.4 mm Hg) was applied. The reaction was continued at 270°C under less than 0.053 kPa (0.4 mm Hg) for 5 hours. The copolyester had an inherent viscosity of 0.87. The glass transition temperature was 64°C. The O₂ and CO₂ gas permeabilities were 7.2×10⁻¹² and 27×10⁻¹² cc-mm/cm²-sec-kPa (1.6 and 6.0 cc./mil per 100 in.²/day/atm.), respectively.

Such copolyesters as described for blending with PET according to the present invention are disclosed in U.S. Patent No. 4,398,017.

25 The polyester-based intimate fusion blend composition comprises admixtures of PET from 80 to 90 weight percent and copolyester from 20 to 10 weight percent. The most preferred copolyester composition useful for admixing with the PET is a copolyester formed by reacting about 90 percent isophthalic acid and about 10 percent terephthalic acid with about 15 percent 1,3 bis(2 - hydroxyethoxy) - benzene, as illustrated in Example 12, such copolyester having a glass transition temperature of about 64°C, a PO₂ of about 7.2 cc-mm/cm²-sec-kPa (about 1.6 cc./mil per 100 in.²/day/atm). and a PCO₂ of about 27 cc-mm/cm²-sec-kPa (about 6.0 cc./mil per 100 in.²/day/atm.) as exemplified above.

30 In the preparation of the virgin blends of the polyester-based intimate fusion blend compositions, the granular or flaked solid polymer is admixed by any conventional means, for example admixed in dry form and subsequent melt fusion blended by passing the granules through a conventional hot melt twin screw-type extruder.

Such material from the extruder can be directly extruded as film. In the alternative, in the preparation of blow-moulded containers from the polyester based intimate fusion blend compositions according to the present invention, typically the material exiting from the above-referred to twin screw hot melt extruder will be forcibly injected into parison moulds to form a parison and cooled to a degree wherein the parison maintains its shape. The parisons can be directly taken, while hot, to a blow moulding station and inflated into oriented or unoriented containers. The parisons can also be cooled and collected for later blow-moulding by the reheat and blow technique.

The preferred orientation temperature for the materials according to the present invention is on the order of 85—110°C.

45 In the case of relatively thick sheet and relatively thin film forming from the polyester based intimate fusion blend compositions according to the present invention, conventional sheet and film forming devices and methods may be used. The material requires no special handling. The thick sheet stock can be converted by thermoforming to produce deep drawn food trays by conventional means while thin films may be extruded, stretch oriented and used as food wraps.

50 The polyester-based intimate fusion blend compositions according to the present invention, in addition to the polymeric components described above, may also contain minor amounts of colourants, inner-fillers, polymerization catalysts, cross-linking agents to improve melt strength, antioxidants, stabilizers, pigments and the like conventionally employed materials as mentioned above for the PET component of the blends.

55 To illustrate the superior gas barrier properties exhibited by the compositions of the present invention for use as sheet stock (useful for thermoformed containers) or thin film (useful for foodwrap), the preferred copolyester composition, exemplified above at Example 12, was admixed with PET at 10 and 20 weight percent of copolyester and 90 and 80 percent PET, respectively, in a conventional twin screw extruder and extruded conventionally into unoriented films. The extruded film was tested using a Mo Con Permatron C film analyzer at 23°C (73°F.), under dry conditions, for CO₂ and O₂ barrier properties.

60 The extruded unoriented film described below in Tables I and II had the following gas permeabilities.

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TABLE I
Carbon dioxide transmission rate for unoriented extruded film

Sample	Composition (wt. percent)	Avg. film thickness		CO ₂ transmission rate at STP		CO ₂ permeability at STP	
		mils	mm	(A)	(B)	(A)	(B)
1	100 PET	13.9	0.353	3.82	17.19	53.1	238.95
2	100 PET	13.5	0.343	3.76	16.92	50.7	228.17
3	100 PET	13.4	0.340	3.75	16.88	50.2	225.90
average		13.6	0.345	3.77	16.97	51.3	230.85
1	90 PET/10 Copolyester	11.8	0.300	3.55	15.98	41.9	188.55
2	90 PET/10 Copolyester	10.8	0.274	3.54	15.93	38.3	172.35
3	90 PET/10 Copolyester	11.8	0.300	3.42	15.39	40.3	181.35
average		11.5	0.292	3.50	15.75	40.2	180.90
Average barrier improvement over 100% PET=22%							
1	80 PET/20 Copolyester	12.6	0.320	2.27	10.22		
2	80 PET/20 Copolyester	11.6	0.295	2.77	12.47		
average		12.1	0.307	2.52	11.34		
Average barrier improvement over 100% PET=41%							
(A) cc/mil per 100 in ² /day/atm							
(B) cc-mm/cm ² -sec-kPa (as×10 ⁻¹²)							

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TABLE II
Oxygen transmission rate for unoriented extruded film

Sample	Compositions (wt. percent)	Avg. film thickness		Oxygen permeability at STP	
		mils	mm	(A)	(B)
1	100 PET	13.9	0.353	8.9	40.05
2	100 PET	13.5	0.343	9.9	44.55
3	100 PET	13.4	0.340	9.5	42.75
average		13.6	0.345	9.4	42.30
1	90 PET/10 Copolyester	11.8	0.300	7.9	35.55
2	90 PET/10 Copolyester	10.8	0.274	7.7	34.65
Average barrier improvement over 100% PET=17%					
1	80 PET/20 Copolyester	12.6	0.320	6.1	27.45
2	80 PET/20 Copolyester	11.6	0.295	7.4	33.30
average		12.1	0.307	6.8	30.60
Average barrier improvement over 100% PET=28%					
(A) cc/mil per 100 in ² /day/atm (B) cc-mm/cm ² -sec-kPa (as×10 ¹²)					

The data of Table I clearly indicates that the polyester based intimate fusion blend composition illustrated is substantially superior to PET in CO₂ barrier properties but do not significantly sacrifice mechanical properties. The 90/10 blends of PET and the preferred copolyester exemplified in Example 12 are about 22 percent better gas barriers to CO₂ transmission than PET. The 80/20 blends of PET and the preferred copolyester of Example 12 are about 41 percent better gas barriers to CO₂ transmission than PET. Unexpectedly, the blends are substantially superior than one would predict. Figure 1 shows the relationship between CO₂ gas transmission versus percentage blends from pure PET to pure copolyesters. The theoretical gas transmission rate is represented by line A while the actual measured value for the blends is illustrated by line B. The actual values for reduced CO₂ transmission are substantially higher than predictable illustrating unexpected results in the blended compositions.

The data of Table II clearly indicates that the polyester based intimate fusion blend composition illustrated is substantially superior to PET in O₂ barrier properties. The 90/10 blends for PET and the preferred copolyester exemplified in Example 12 are about 17 percent better gas barriers to CO₂ transmission than PET. The 80/20 blends of PET and the preferred copolyester of Example 12 are about 28 percent better gas barriers to O₂ transmission than PET. Unexpectedly, the blends are substantially superior than one would predict. Figure 2 shows the relationship between O₂ gas transmission versus percentage blends from pure PET to pure copolyesters. The theoretical gas transmission rate is represented by line A while the actual measured value for the blends is illustrated by line B. The actual values for reduced O₂ transmission are substantially higher than predictable illustrating unexpected results in the blended compositions.

Another important property of materials used for food and beverage packaging is the water vapour transmission rate.

Table III below illustrates the superior water vapour barrier characteristics of the present composition. The compression moulded samples of unoriented material are fabricated from the preferred composition of Example 12 admixed with the specified amounts of PET and are tested. The water vapour transmission and water vapour permeability are determined gravimetrically using a commercially available Thwing-Albert cup at 23°C (73°F.) at relative humidities between 50—100%.

The compression moulded samples described below in Table III had the following water vapour transmission rates and water vapour permeability rates.

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TABLE III
Water barrier properties for unoriented film

Sample	Composition (wt. percent)	Avg. film thickness		Water vapour transmission		Water vapour permeability	
		mils	mm	(C)	(D)	(E)	(F)
1	100 PET	13.7	0.348	0.077	2.07	1.05	1.538
2	100 PET	12.6	0.320	0.078	2.10	0.97	1.421
3	100 PET	13.4	0.340	0.075	2.02	1.00	1.465
Average		13.2	0.335	0.077	2.07	1.01	1.479
1	90 PET/10 Copolyester	11.6	0.295	0.071	1.91	0.825	1.208
2	90 PET/10 Copolyester	10.7	0.272	0.082	2.20	0.872	1.277
3	90 PET/10 Copolyester	11.8	0.300	0.076	2.04	0.898	1.315
Average		11.3	0.287	0.076	2.04	0.865	1.267
Average water barrier improvement over 100% PET=14%							
1	80 PET/20 Copolyester	12.9	0.328	0.054	1.45	0.700	1.025
2	80 PET/20 Copolyester	11.2	0.284	0.068	1.83	0.760	1.113
Average		12	0.305	0.061	1.64	0.730	1.069
Average water barrier improvement over 100% PET=28%							
(C) 100 sq in/day							
(D) cm ² /hour							
(E) $\frac{\text{g/mils}}{100 \text{ sq in/day}}$							
(F) $\frac{\text{g/mn}}{\text{cm}^2/\text{hour}}$							

The data of Table III clearly indicates that the polyester based intimate fusion blend compositions illustrated is significantly superior to PET in water barrier properties. The 90/10 blends of PET and the preferred copolyester exemplified in Example 12 are about 14 percent better water barriers than PET. The 80/20 blends of PET and the preferred copolyester of Example 12 are about 28 percent better in water barrier properties than PET.

To demonstrate that the compositions according to the present invention show significantly improved carbon dioxide, water and oxygen barrier properties but does not significantly sacrifice mechanical properties, compression moulded films were tested to determine the important mechanical properties of elastic modulus, yield stress, yield strain, ultimate strength and ultimate elongation. The results are set forth below and are, as before, for PET-copolyester blends employing the preferred copolyester of Example 12.

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TABLE IV
Mechanical properties of unoriented film

Property		100 PET	Composition (wt. percent)	
			90 PET-10 Copolyester	80 PET 20 Copolyester
Elastic modulus kPa (PSI×1000)	average	2151 (312)	2310 (335)	2372 (344)
	deviation	62 (9)	55 (8)	103 (15)
Yield stress kPa (PSI×1000)	average	54.5 (7.9)	59.3 (8.6)	64.1 (9.3)
	deviation	0.7 (0.1)	2.1 (0.3)	1.4 (0.2)
Yield strain in Percent	average	3.4	3.4	3.5
	deviation	0.2	0.2	0.2
Ultimate strength kPa (PSI×1000)	average	66.2 (9.6)	51.7 (7.5)	51.0 (7.4)
	deviation	9.0 (1.3)	4.8 (0.7)	6.9 (1.0)
Ultimate elongation in percent	average	326	245	231
	deviation	61	28	55

Each test was completed using five different specimens with a stretch rate of 0.51 cm (0.2 inches) per minute and under conditions of ASTM test 1822.

Note that both the 90/10 and 80/20 blends of PET and copolyester according to the invention maintain or show improved elastic modulus, yield stress and yield strain compared to 100 percent PET and sacrifice only slightly in ultimate strength and ultimate elongation.

Quite unexpectedly, overall the composition exemplified above according to the present invention maintains most mechanical properties and show significantly improved barrier properties.

As pointed out above, the polyester-based intimate fusion blend compositions according to the present invention are well-suited for the formation of thermoplastic container parisons and the resulting containers, which containers may occur in multiple embodiments.

Figure 3 is a perspective view of a thermoplastic parison according to the present invention wherein the parison 10 includes a threaded finish portion 12, an outstanding handling ledge 14 depending downwardly from and integral with the threaded finish portion 12, a main body portion 16 depending downwardly from and integral with the handling ledge 14 and a closed bottom portion 18 integral with and downwardly depending from the main body portion 16. The parison 10 is conveniently formed by well-known injection moulding techniques using the polyester-based intimate fusion blend composition according to the present invention without any special conditions or equipment requirements.

The parison illustrated in Figure 3 may be blow-moulded by conventional blow-moulding techniques to form a first embodiment of the container according to the present invention as shown at Figure 4 represented by the bottle 20. The bottle 20 includes a threaded finish portion 22, a handling ledge 24, which is integral with and downwardly depending from the threaded finish portion 22 and further includes an outwardly sloping shoulder portion 26 which is integral with and downwardly depending from the handling ledge 24. A main body portion 28 is integral with and downwardly depending from the shoulder 26. A closed bottom portion 30 is formed integral with and downwardly depending from the main body portion 28 and serves to completely close the bottom of the bottle 20.

An alternative embodiment of a container according to the present invention which can be made from extruded sheet formed of the polyester-based intimate fusion blend composition according to the present invention is illustrated at Figure 5 by a deep-drawn food tray 32. The food tray 32 includes a flat upper sealing rim 34 which is typically a substrate upon which a conventional foil closure is sealed with conventional adhesives to form a closed package for containing foodstuffs. Downwardly depending from and integral with the sealing rim 34 are a plurality of interconnecting side panels, namely the side panels 36, 38, 40 and 42. A centrally located bottom portion 44 is formed integral with and generally perpendicular to the interconnected side panels 36, 38, 40 and 42 to form a completely sealed bottom portion of the food tray 32.

Claims

1. A composition characterised by:
an intimate fusion blend of:

(1) 80 to 90 weight per cent of a poly(ethylene terephthalate); and

(2) 10 to 20 weight per cent of a copolyester formed of the polymeric reaction product of,

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- (A) reactant(s) selected from isophthalic acid, terephthalic acid, and their C₁ to C₄ alkyl esters, and any mixture thereof in any proportion,
- (B) reactants, 1,3 bis(2 - hydroxyethoxy)benzene plus ethylene glycol, wherein the amount of the 1,3 bis(2 - hydroxyethoxy)benzene is 5 to 90 mole percent of the amount of (A) reactants.
- 5 2. A composition according to claim 1, wherein the amount of the 1,3 bis(2 - hydroxyethoxy)benzene is 10 to 80 mole percent of the amount of (A) reactants.
3. A composition according to claim 1 or 2, wherein reactants (B) also comprise one or more other ester forming dihydroxy organic hydrocarbon reactants.
4. A composition according to claim 3, wherein the amount of the other ester forming dihydroxy organic reactant(s) is up to 20 mole percent of the amount of the (A) reactant(s).
- 10 5. A composition according to claim 4, wherein the amount of the other ester forming dihydroxy organic reactant(s) is up to 15 mole percent of the amount of the (A) reactant(s).
6. A composition according to any of claims 1 to 5, wherein the reactants to form copolyester (2) also comprise:
- 15 (C) bis(4 - beta - hydroxyethoxy - phenyl) sulfone, and wherein
- (1) the combined amount of (B) and (C) reactants is about 110 to 300 mole percent of the amount of (A) reactant(s), and
- (2) the combined amount of the (C) reactant and the 1,3 bis(2 - hydroxyethoxy)benzene, and of the other ester forming dihydroxy organic reactant(s) when present, is not over 90 mole percent of the (A) reactant(s).
- 20 7. A composition according to any of claims 1 to 6, wherein the poly(ethylene terephthalate) (1) is selected from polymers wherein at least 97% of the polymer contains the repeating ethylene terephthalate units with the remainder being minor amounts of ester-forming components, and copolymers of ethylene terephthalate wherein up to about 10 mole percent of the polymer is prepared from other diol monomer units substituted for the glycol moiety in the preparation of the polymer or other dicarboxylic acid monomer units substituted for up to 10 mole percent of the acid moiety in the preparation of the polymer.
- 25 8. A sheet or film characterised by having the composition according to any of claims 1 to 7.
9. A deep drawn tray characterised by having the composition according to any of claims 1 to 7.
10. A container comprising:
- 30 (a) an open top portion;
- (b) an enclosed main body portion integral with and downwardly depending from the open top portion; and
- (c) an enclosed bottom portion integral with and downwardly depending from the enclosed main body portion, characterised in that the container is fabricated from an intimate fusion blend according to any of claims 1 to 7.
- 35 11. A container preform comprising:
- (a) a threaded finish portion;
- (b) a main body portion integral with and downwardly depending from the threaded finish portion; and
- (c) a closed bottom portion integral with and downwardly depending from said main body portion, characterised in that the preform is fabricated from an intimate fusion blend according to any of claims 1 to 7.
- 40 7.

Patentansprüche

- 45 1. Zusammensetzung, gekennzeichnet durch eine innige Schmelzmischung von:
- (1) 80 bis 90 Gew.-% an Poly(ethylenterephthalat); und
- (2) 10 bis 20 Gew.-% eines Copolyesters, der das Reaktionsprodukt einer Polymerisationsreaktion von,
- (A) Reaktionsmittel(n) ausgewählt aus der Gruppe der Isophthalsäure, Terephthalsäure und ihrer C₁ bis C₄ Alkylester sowie jeder Mischung davon in jedem Mengenverhältnis,
- 50 (B) Reaktionsmitteln, 1,3 - bis(2 - Hydroxyethoxy)benzol plus Ethylenglycol, wobei der Gehalt von dem 1,3 - bis(2 - Hydroxyethoxy)benzol zwischen 5 und 90 Mol-% des Gehaltes der (A)-Reaktionsmittel beträgt.
2. Zusammensetzung nach Anspruch 1, in der der Gehalt des 1,3 - bis(2 - Hydroxyethoxy)benzols zwischen 10 bis 80 Mol-% des Gehaltes der (A)-Reaktionsmittel beträgt.
- 55 3. Zusammensetzung nach den Ansprüchen 1 oder 2, in der die (B)-Reaktionsmittel weiterhin ein oder mehrere Ester bildende Reaktionsmittel in Form von organischen Dihydroxykohlenwasserstoffen enthält.
4. Zusammensetzung nach Anspruch 3, in der der Gehalt des (der) weiteren Ester bildenden, organischen Dihydroxyreaktionsmittel(s) bis 20 Mol-% des Gehaltes des (der) (A)-Reaktionsmittel(s) beträgt.
- 60 5. Zusammensetzung nach Anspruch 3, in der der Gehalt des (der) weiteren, Ester bildenden organischen Dihydroxyreaktionsmittel(s) bis zu 15 Mol-% des Gehaltes des (der) (A) - Reaktionsmittel(s) beträgt.
6. Zusammensetzung nach einem der Ansprüche 1 bis 5, in der die Reaktionsmittel zur Bildung des Copolyesters (2) weiterhin enthalten:
- 65 (C) bis(4 - beta - Hydroxyethoxy - phenyl) - sulfon und in der

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(1) der vereinigte Gehalt von (B) und (C) Reaktionsmitteln zwischen etwa 110 bis 300 Mol-% des Gehaltes des (der) (A) - Reaktionsmittel(s) beträgt, und

(2) der vereinigte Gehalt des (C)-Reaktionsmittel und 1,3 bis(2 - Hydroxyethoxy) - benzol und, falls vorhanden, des (der) weiteren, Ester bildenden, organischen Dihydroxyreaktionsmittel(s) nicht mehr als 90 Mol-% des (der) (A) - Reaktionsmittel(s) beträgt.

7. Zusammensetzung nach einem der Ansprüche 1 bis 6, bei der das Poly(ethylenterephthalat) (1) aus Polymeren, bei denen mindestens 97% des Polymers die sich wiederholenden Ethylenterephthalat-einheiten enthält, wobei der Rest durch geringe Anteile von Ester bildenden Komponenten gebildet wird, und Ethylenterephthalatcopolymeren ausgewählt wird, bei denen bis zu 10 Mol-% des Polymeres mit anderen Diolmonomereinheiten, die während der Herstellung des Polymers für die Glycolteile substituiert werden oder anderen Dicarbonsäuremonomereinheiten hergestellt wird, bei denen bis zu 10 Mol-% des Säureteils während der Herstellung des Polymers substituiert werden.

8. Folie oder Film, dadurch gekennzeichnet, daß ihre oder seine Zusammensetzung einem der Ansprüche 1 bis 7 entspricht.

9. Tiefgezogene Schale, dadurch gekennzeichnet, daß sie eine Zusammensetzung nach einem der Ansprüche 1 bis 7 aufweist.

10. Behälter mit:

- (a) einem geöffneten oberen Teil;
- (b) einem umschlossenen Zentralteil, der eine Einheit mit dem oberen geöffneten Teil bildet und von diesem nach unten weisend angeordnet ist; und
- (c) einem umschlossenen Bodenteil, der mit dem umschlossenen Zentralteil eine Einheit bildet und von diesem nach unten weisend angeordnet ist, dadurch gekennzeichnet, daß der Behälter aus einer innigen Schmelzmischung nach einem der Ansprüche 1 bis 7 hergestellt wird.

11. Eine Behältervorform mit:

- (a) einem mit einem Gewinde versehenen Abschlußteil;
- (b) einem Zentralteil, der eine Einheit mit dem Gewindeabschlußteil bildet und von diesem nach unten weisend angeordnet ist; und
- (c) einem geschlossenen Bodenteil, der eine Einheit mit dem Zentralteil bildet und von diesem nach unten weisend angeordnet ist, dadurch gekennzeichnet, daß die Vorform aus einer innigen Schmelzmischung nach einem der Ansprüche 1 bis 7 hergestellt wird.

Revendications

1. Une composition caractérisée par:
un mélange par fusion intime de:

- (1) 80 à 90 pourcent en poids d'un poly(téréphtalate d'éthylène); et
- (2) 10 à 20 pourcent en poids d'un copolymère formé par le produit de polymérisation de: réactif(s) (A) choisi(s) parmi: acide isophtalique, acide téréphtalique et leurs esters d'alkyle en C₁ à C₄, ainsi que tout mélange de ceux-ci en toutes proportions,

réactifs (B), 1,3bis(2-hydroxyéthoxy)benzène plus éthylène-glycol, dans lequel la quantité de 1,3bis(2 - hydroxyéthoxy)benzène représente 5 à 90 moles pourcent de la quantité de réactifs (A).

2. Une composition selon la revendication 1, dans laquelle la quantité de 1,3bis(2 - hydroxyéthoxy)-benzène représente 10 à 80 moles pourcent de la quantité de réactifs (A).

3. Une composition selon la revendication 1 ou 2, dans laquelle les réactifs (B) comprennent également un ou plusieurs autres réactifs estérifiables de type hydrocarbure organique dihydroxylé.

4. Une composition selon la revendication 3, dans laquelle la quantité d'(des) autre(s) réactif(s) organique(s) dihydroxylé(s) estérifiable(s) représente jusqu'à 20 moles pourcent de la quantité de réactif(s) (A).

5. Une composition selon la revendication 4, dans laquelle la quantité d'(des) autre(s) réactif(s) organique(s) dihydroxylé(s) estérifiable(s) représente jusqu'à 15 moles pourcent de la quantité de réactif(s) (A).

6. Une composition selon l'une quelconque des revendications 1 à 5, dans laquelle les réactifs devant former le copolymère (2) comprennent également:

la bis(4-bêta-hydroxyéthoxy-phényl)sulfone (C), et dans laquelle:

- (1) les quantités réunies des réactifs (B) et (C) représentent environ 110 à 300 moles pourcent de la quantité de réactif(s) (A), et
- (2) les quantités réunies de réactif (C), de 1,3 - bis(2 - hydroxyéthoxy)benzène et, le cas échéant, d'(des) autre(s) réactif(s) organique(s) dihydroxylé(s) estérifiable(s), ne représentent pas plus de 90 moles pourcent de(s) réactif(s) (A).

7. Une composition selon l'une quelconque des revendications 1 à 6, dans laquelle le poly(téréphtalate d'éthylène) (1) est choisi parmi des polymères dans lesquels au moins 97% du polymère contient les motifs téréphtalate d'éthylène répétés, le reste étant constitué par de faibles quantités de composés estérifiables, et parmi des copolymères de téréphtalate d'éthylène dans lesquels jusqu'à environ 10 moles pourcent du polymère est élaboré à partir d'autres éléments diols monomères, substitués à la partie glycolique lors de

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la préparation du polymère, ou d'autres éléments acides dicarboxyliques monomères, substitués, à un taux allant jusqu'à 10 moles pourcent, à la partie acide lors de la préparation du polymère.

8. Une feuille ou un film, caractérisé par sa composition conforme à l'une quelconque des revendications 1 à 7.

5 9. Une barquette caractérisée par sa composition conforme à l'une quelconque des revendications 1 à 7.

10. Un récipient comprenant:

(a) une partie supérieure ouverte

10 (b) une partie fermée formant le corps principal, d'une seule pièce avec la partie supérieure ouverte et rattachée à l'extrémité inférieure de cette dernière; et

(c) une partie fond fermée, d'une seule pièce avec la partie fermée formant le corps principal et rattachée à l'extrémité inférieure de cette dernière, caractérisé en ce que le récipient est élaboré à partir d'un mélange par fusion intime selon l'une quelconque des revendications 1 à 7.

11. Une ébauche de récipient comprenant:

15 (a) une partie filetée terminale;

(b) une partie formant le corps principal, d'une seule pièce avec la partie filetée terminale et rattachée à l'extrémité inférieure de cette dernière; et

20 (c) une partie fond fermée, d'une seule pièce avec ladite partie formant le corps principal et rattachée à l'extrémité inférieure de cette dernière, caractérisée en ce que l'ébauche est élaborée à partir d'un mélange par fusion intime selon l'une quelconque des revendications 1 à 7.

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FIG. 1

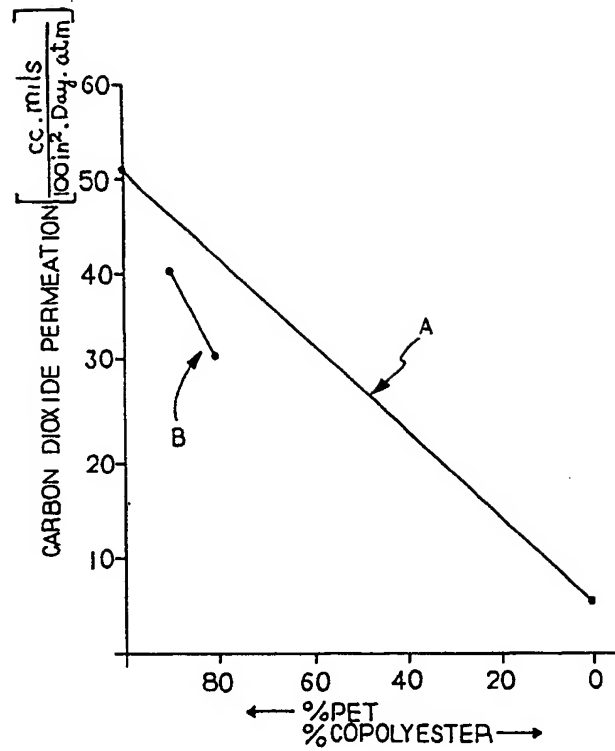
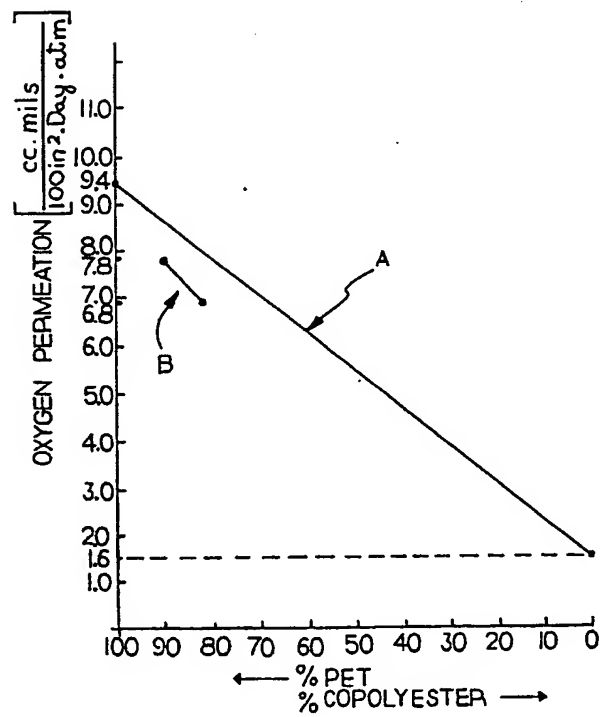


FIG. 2



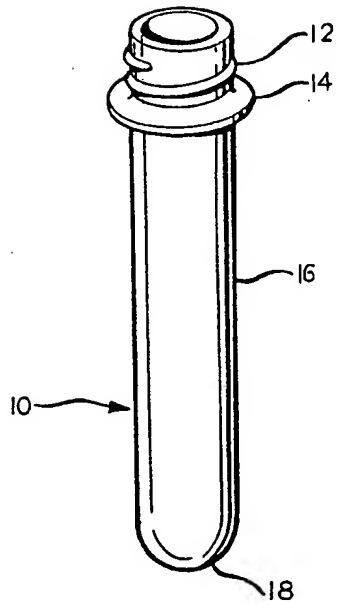


FIG. 3

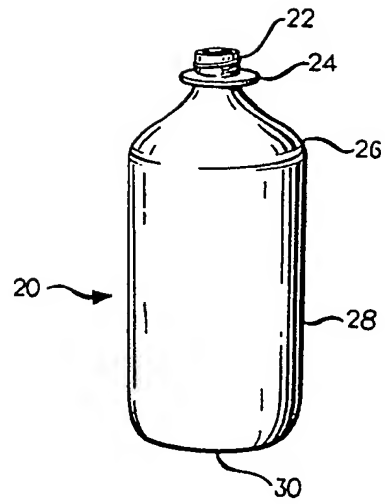


FIG. 4

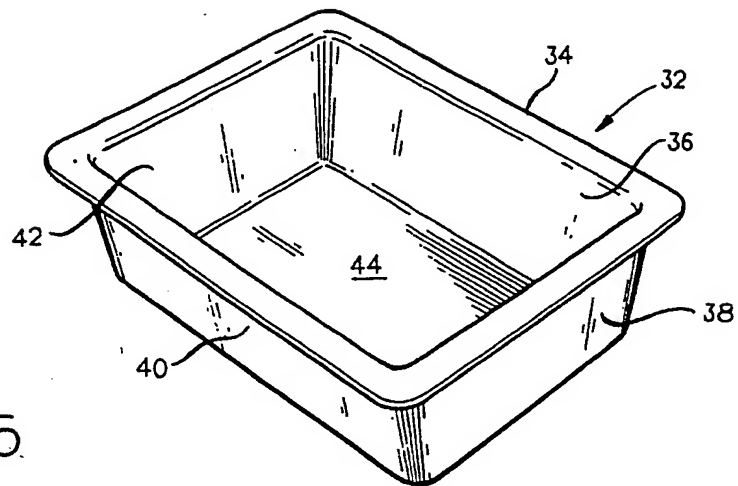


FIG. 5

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